Random and ordered phases of off-lattice rhombus tiles

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We study the covering of the plane by non-overlapping rhombus tiles. This problem is well-studied only in the limiting case of regular rhombi constrained by an underlying lattice (equivalent to the problem of dimer coverings of regular lattices). Here we go beyond this limit by allowing tiles to take any position and orientation on the plane, to be of irregular shape, and to possess different types of attractive interactions. Using extensive numerical simulations we show that at large tile densities there is a solidification transition from a fluid of rhombus tiles to a solid packing with broken rotational symmetry. We observe self-assembly of broken-symmetry phases, even at low densities, in the presence of attractive tile-tile interactions. Depending on tile shape and interactions the solid phase can be random, possessing critical orientational fluctuations, or crystalline. We predict novel behaviors that might be realized through the self-assembly of 'molecular rhombi'.

Introduction. The use of two-dimensional molecular networks to control the chemical and physical functionalities of semiconductor, metallic and graphite surfaces shows great promise for technology [1, 2]. Molecular networks also provide fascinating problems of fundamental science. While much of the work in this area focuses on the self-assembly of ordered molecular arrays, recent work shows that two-dimensional glassy systems can be formed by small organic molecules [3–5]. These glassy arrays are characterised by the absence of long-range translational symmetry, and one such system (composed of p-terphenyl-3,5,3",5"-tetracarboxylic acid, or TPTC, molecules) can be mapped onto a rhombus tiling. The latter problem is a classic one of statistical mechanics [6–14], and one can show that the molecular array adopts a configuration of maximum entropy. However, this mapping relies on two assumptions that motivate an alternative approach. The first assumption is that the rhombus tiling is constrained by an underlying triangular lattice. The second is that tiles can effect a complete dimer covering of this lattice, i.e. that TPTC can be represented as what we will call a *regular* rhombus whose internal angles are 60° and 120°. In reality, the graphite lattice used in experiment supports multiple registries and orientations of the molecular overlayer, and molecules do not possess exactly the aspect ratio of the regular rhombus.

These observations motivate a theoretical approach to rhombus tilings that relaxes these constraints: tiles need not be regular rhombi, and they can be placed in any position and with any orientation on the plane. This is the problem we study here by means of computer simulations. We first show that regular rhombi will tile the plane randomly, by packing parallel or at 60°, in a manner similar to their on-lattice counterparts (in snapshots, rhombi are colored according to their absolute orientations). Motivated by recent experiments, we then show that hydrogen bond-like interactions induce the regular rhombus to self-assemble into a random tiling, and identify the geometric limits beyond which tile self-assembly results in ordered phases. We make predictions for novel behaviors that might be realized through the self-assembly of 'molecular rhombi'.

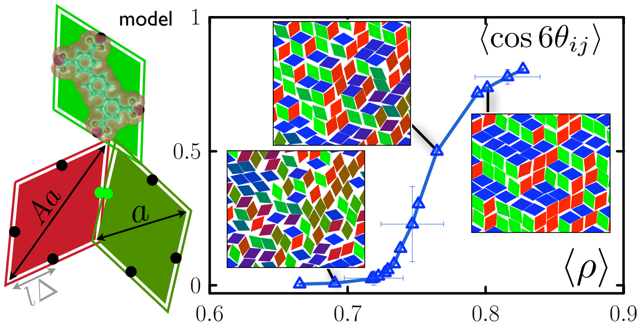

FIG. 1: Off-lattice rhombi tile the plane: equilibrated constant-pressure simulations of hard rhombi of aspect ratio $A = \sqrt{3}$ show the emergence of long range hexatic order at densities ρ above about 70%. Left: model geometry, overlaid by isosurface of TPTC ground-state electron density.

Model and simulation details. We simulated the packing and self-assembly of hard rhombi with a long-to-short diagonal aspect ratio A (see Fig. 1, left) on a featureless two-dimensional substrate; the regular rhombus with internal angles 60° and 120° has $A = \sqrt{3}$. The short diagonal length a is typically 1 nm for the molecules studied experimentally. Such molecules interact via hydrogen bonding, which is highly directional. To model such an interaction we equipped rhombi with specific interactions mediated by patches placed on each edge a distance $l\Delta$ from the small internal angle (l is edge length); patches on adjacent rhombi give rise to an energetic reward of $-\epsilon_{\rm s}\, k_{\rm B}T$ if they approach closer than a distance $a/10$. To assess the importance of interaction specificity we also considered, in Fig. 5, a rhombus-shaped nonspecific force-field of identical aspect ratio and small diagonal length

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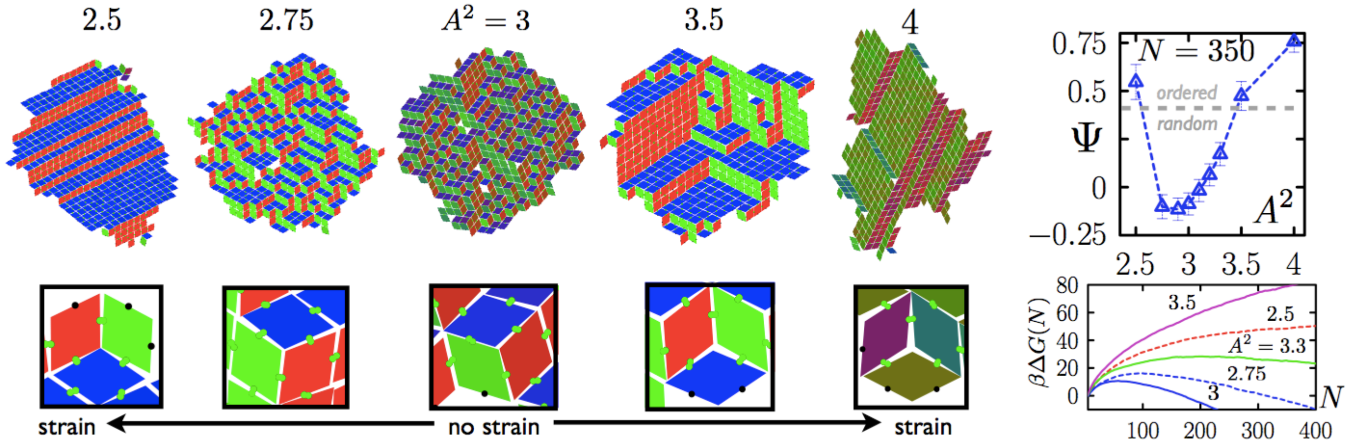

FIG. 2: Rhombus tiles with attractive 'H-bond' interactions self-assemble into random- and ordered solid phases. Regular rhombi ($A = \sqrt{3}$) assemble as a random solid; sufficiently irregular rhombi form the parallel ordered one (see top right). Snapshot enlargements show that the ordered phase emerges when the 3-particle 'boxes' required to form the random tiling become geometrically strained.

$a_0 = 11a/10$ (see particle 'halo' in Fig. 1, inset): the overlap of two forcefields triggers a pairwise energetic reward of $-\epsilon_{\rm n}\, k_{\rm B}T$.

We used a collection of Monte Carlo algorithms to study tiling thermodynamics and dynamics. Simulation boxes were rhombus-shaped and periodically replicated in imitation of bulk surroundings. To study the packing of hard rhombi (Fig. 1) we used standard constant-pressure moves, single-particle Metropolis translations and rotations [15], and the following 3-particle rotation algorithm. Starting from microstate 1 (say), we selected at random a tile i, and then selected at random any two tiles able to interact with it through the specific interaction (even though $\epsilon_{\rm s} = 0$). We call such particles 'H-bonded neighbors'. If fewer than two such neighbors existed, the move was aborted. Otherwise, we rotated our three chosen particles by 60° (with either sense) about their center of mass, defining a proposed new microstate 2. We accepted this rotation with probability $\min(1, n_1(n_1-1)/[n_2(n_2-1)]\exp(-\beta\Delta E))$. The variable n_1 is the number of H-bonded neighbors possessed by tile i in microstate 1; the factor it appears in accounts for the fact that tile i might have a different number of H-bonded neighbors following the proposed rotation. The term ΔE is the change of energy following the move. This algorithm allows efficient conversion between ordered and random dense tilings.

To study the self-assembly of clusters of interacting rhombi (Fig. 2) we used standard umbrella sampling of the size of a growing cluster [15, 16] in conjunction with single-particle moves, the virtual-move algorithm [17] of Ref. [18] (to allow collective rearrangements of tilings), the 3-particle rotation algorithm, and grand canonical insertions and deletions of rhombi at constant chemical potential μ [15]. Two-species nucleation simulations (Fig. 4) were done using an umbrella sampling protocol in which deposited particles were chosen to be of type A with likelihood $C_0 \leq 1$; species-interconversion moves were proposed randomly and accepted with probability $\min(1, \exp[-\beta(\Delta E + \Delta E_{\rm s})])$, where $\Delta E_{\rm s} = \mp k_{\rm B}T \ln\left(C_0^{-1} - 1\right)$. The interconversion of dense tilings (Fig. 5a) was studied using the three-particle rotation algorithm, and dynamic simulations of rhombus self-assembly (Fig. 5b) were done using grand-canonical moves and the virtual-move algorithm.

We characterized solid order using the parameter $\Psi \equiv (0.608 n_{\parallel} - 0.392 n_{\nparallel})/(0.608 n_{\parallel} + 0.392 n_{\nparallel})$. Here $n_{\parallel}$ is the total number (within the simulation box or the largest cluster, as appropriate) of H-bonds between particles whose long diagonals lie closer to being parallel than nonparallel. $n_{\nparallel}$ is the total number of all other H-bonds. This order parameter allows us to distinguish random tiled structures ($|\Psi| \approx 0$) from crystalline structures with parallel order ($\Psi \lesssim 1$) or nonparallel order ($\Psi \gtrsim -1$; see Fig. S1 for examples of these phases). These distinct solid phases are expected theoretically [11] for on-lattice interacting rhombi, and have been observed experimentally [19].

We also carried out density functional theory (DFT) calculations [20] of TPTC in vacuum (Figs. 1 and 3) using the B3LYP [21] functional and the the 6-311+G* basis set. This basis set includes both diffuse and polarization functions.

Results. We show in Fig. 1 the results of constant pressure simulations of 768 noninteracting ($\epsilon_{\rm n} = \epsilon_{\rm s} = 0$) regular rhombi. We plot as a function of density the thermal average of the hexatic order parameter $\cos(6\theta_{ij})$, where θ_{ij} is the angle between vectors pointing along the long diagonals of rhombi i and j. The average is taken over all pairs of particles. Long range hexatic order

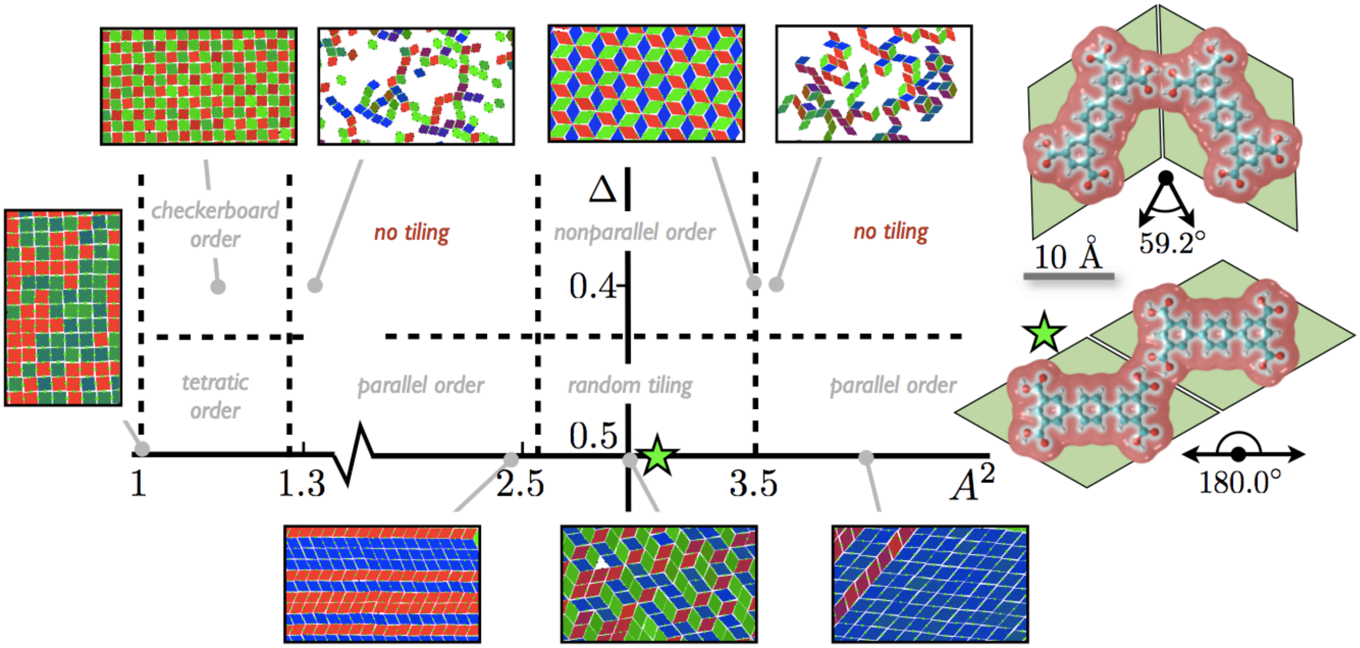

FIG. 3: Design space of 'molecular rhombi'. Schematic phase diagram of aspect ratio A and patch placement Δ (phase boundaries are approximate). DFT calculations reveal that TPTC (right) corresponds to a nearly-regular rhombus whose patches are placed near-centrally.

emerges at densities of about 70%; such order is consistent with a tiling in which particles point in the three directions of a triangular lattice [25] (simulation box snapshots are shown in Fig. S2). Notably, the high-density solid phase is not crystalline but random, possessing a value of $\Psi \approx 0$ [26]. It has a high degree of orientational order but no translational order. The random phase is known from theoretical studies to possess critical fluctuations in tile orientation characteristic of entropically-stabilized 'Coulomb phase' systems [9]. Random tilings are seen in the standard limiting case of regular rhombi constrained to an underlying triangular lattice; the spontaneous emergence of similar order here, driven only by rhombus shape, justifies the approximations inherent in that limiting case.

We next verified that equipping rhombi with symmetric ($\Delta = 1/2$) 'H-bond' interactions allows them to self-assemble, even at low densities, into a random tiling. In Fig. 2 we show results from simulations in which interacting rhombi ($\epsilon_{\rm s} = 5.2$) were allowed to deposit on a substrate, with μ chosen so that a dense cluster of regular rhombi faced a free energy barrier of about 10 $k_{\rm B}T$ to its nucleation. Nuclei were grown using umbrella sampling. Nuclei of regular rhombi have a value of Ψ slightly less than zero, showing them to be random [22] but with a slight bias for the nonparallel binding mode. This bias results from a small difference in inter-patch distances for parallel- and nonparallel binding within an orientationally ordered tiling, and can be annulled by shifting patches slightly towards the small internal angle (a large shift drives the emergence of nonparallel order; see Fig. S3). Notably, assemblies display the topologically interesting triangular defects seen in real networks [4] (a resulting tiling is shown in Fig. S4).

However, perturbing the aspect ratio of rhombi away from the regular value of $A = \sqrt{3}$ impairs their ability to form a random tiling. In Fig. 2 we show that near-regular rhombi can still form clusters having values of Ψ close to zero. But sufficiently irregular rhombi favor the parallel ordered phase, characterized by large positive Ψ. The geometrical reason for the emergence of this phase is shown in the bottom panel of Fig. 2: the random phase contains 3-particle 'boxes' of rhombi that knit together domains of parallel tiles. Boxes form readily when the large internal angle of the rhombus is 120°, but departures from this angle strain boxes and eventually suppress their formation, driving the emergence of a parallel ordered phase. Suppressing box formation also increases the work of formation (bottom right) of a cluster of N tiles.

The design space of 'molecular rhombi' therefore admits ordered and random tiled phases, as sketched in Fig. 3. TPTC is well 'designed' as a random-tiling agent. DFT calculations show binding modes that are parallel and 59.2° disposed, consistent with a rhombus aspect ratio $A \approx \sqrt{3.1}$. Based on an isosurface of ground-state electron density, TPTC's effective patch position Δ for these motifs is 0.50, with a width $\delta\Delta \approx 0.37$. We verified both on- and off-lattice that the calculated slight (0.008 eV) energetic preference in favor of parallel binding does

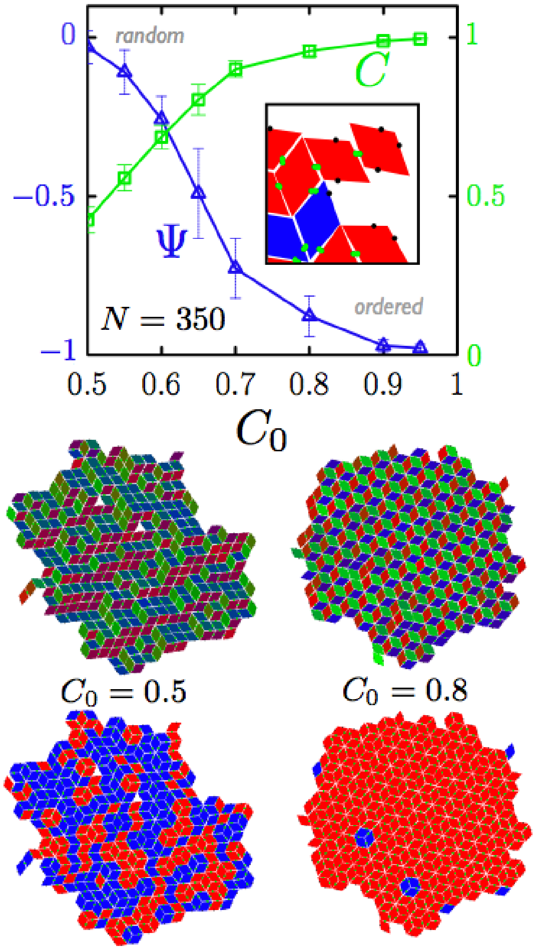

FIG. 4: Prediction for achieving assembly of random- or ordered tilings through variation of tile concentration. Regular rhombi of type A (red, patch position $\Delta_{\mathrm{A}} = 0.55$) and B (blue, patch position $1 - \Delta_{\mathrm{A}}$) are present in solution at relative concentration $C_0/(1 - C_0)$. Because of geometric constraints, in space-filling tilings *intra*-species parallel contacts are strained, while *inter*-species parallel contacts are not (snapshot inset shows the exaggerated case $\Delta_{\mathrm{A}} = 0.7$). By varying relative tile concentrations we find spontaneous assembly of a random tiling when $C_0 \approx 0.5$, and of an ordered tiling when the system is A-rich ($C_0 \lesssim 1$). Snapshots colored by orientation and species (red/blue) for two concentrations. Ψ, C are tiling order and species composition of clusters of fixed size.

not destroy the random tiling. In the square limit $A = 1$, tiling order is tetratic rather than hexatic, and we predict the existence of a 'checkerboard' phase. We also predict the breakdown of order: tiles cannot form dense assemblies when aspect ratio and patch placement are chosen such that tile shape favors, but patch placement cannot accommodate, parallel binding. This conflict defines the geometric limits within which molecular rhombi tile, with the proviso that the precise location of these limits will depend on the ratio of molecular size and the range of H-bond interactions, which we have represented only roughly.

From these findings we can make a prediction for experiment. Fig. S3 reveals that shifting molecules' H-bond patches toward the large internal angle strains (and eventually forbids) the parallel mode of binding in a space-filling tiling. However, a second molecular species with patches shifted an equal distance toward the small internal angle can, without strain, bind parallel to the first species in a dense tiling. We show in Fig. 4 that such mixtures self-assemble into a random tiling when molecules are present in equal number, but assemble into ordered tilings when one species predominates. Thus we predict that by varying only relative concentrations of appropriately-designed molecules, one can induce a phase transition between random and crystalline tilings.

Real molecules also possess interactions, such as van der Waals- or solvent-mediated forces, that are less specific than hydrogen bonding. We have not represented such effects, but we cannot rule out the importance for tiling of interactions other than H-bonds. For example, we show in Fig. 5 that a short-range rhombus-shaped attraction effects a bias in favor of a nonparallel ordered tiling [27]. Through this nonspecific interaction, rhombi 'see' energetically their neighbors at each vertex in a tiling. In tilings with perfect nonparallel order each rhombus has ten such neighbors, five at each corner of its long diagonal (inset bottom left). In a random tiling, rhombi have fewer vertex neighbors (inset top right), and a strong enough nonspecific interaction induces a phase transition from the random phase to the ordered one (the peaked line is the variance of Ψ, scaled and shifted to fit on the plot). We verified in off-lattice simulations that such an attraction can induce a nonparallel bias in tilings of regular rhombi (with or without H-bond interactions), and induce irregular rhombi to form patterns unlike any of the known dense rhombus tilings (Fig. 5b). Without intending to imply that this simple interaction is a realistic representation of intermolecular forces, we conjecture that experimental factors *other* than molecule shape and H-bond placement may be exploited in order to select tiling order.

We have explored rhombus tilings beyond the standard limit of dimer coverings of the regular lattice, identifying physical mechanisms that lead to the emergence of ordered and random phases. We have made predictions for novel behaviors that might be realized using 'molecular rhombi'. The methods described here can be used to study the packing and self-assembly of a wide variety of tiles, aiding the search for molecular networks that possess interesting properties such as quasicrystalline order [23].

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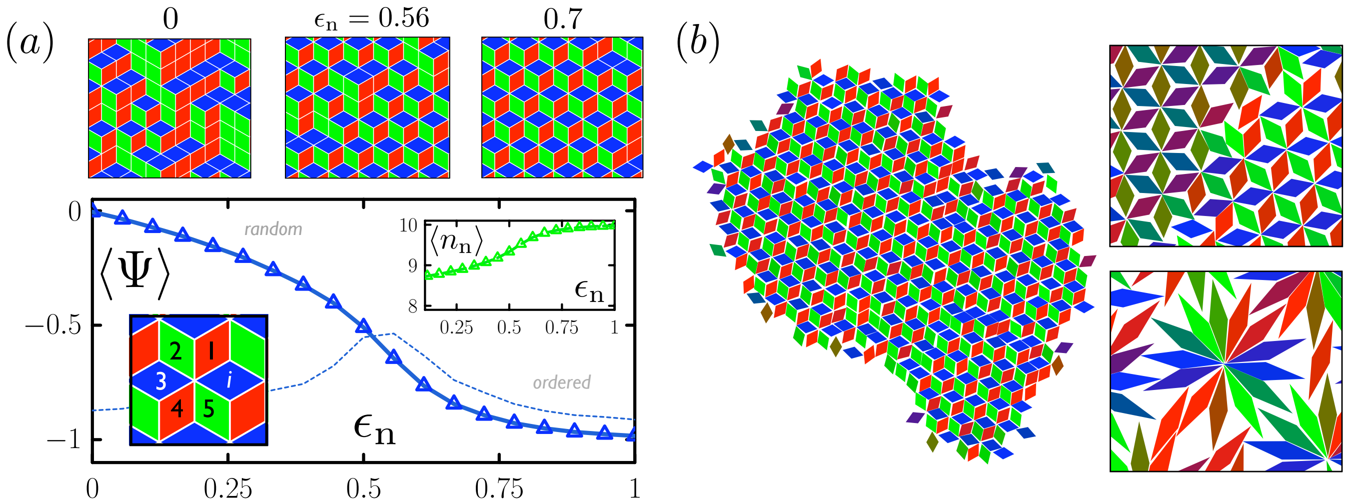

FIG. 5: (a) Interactions other than H-bond attractions may act to select tiling phases. We consider regular rhombi interacting nonspecifically (see text) initially arranged as a random tiling of a triangular lattice. We plot the thermal average of the tiling order parameter Ψ as a function of ϵ_n, the strength of the nonspecific attraction. This attraction favors high-order vertices of the kind found readily in the nonparallel ordered tiling (inset bottom left: particle i has two lots of five vertex neighbors), and if strong enough it destabilizes the random tiling. Inset top right: average number n_n of pairwise nonspecific interactions made by particles. (b) Self-assembly of regular and irregular rhombi driven by the nonspecific interaction. We show configurations taken from dynamical trajectories of rhombi equipped with nonspecific attractions of fixed strength, for the cases $A^2 = 3, 5, 20$ (clockwise from left). The nonspecific attraction favors the formation of tiling vertices, which for the regular rhombus leads to the emergence of the nonparallel ordered tiling ($\Psi \approx -0.7$, left). However, as A departs enough from $\sqrt{3}$ the dense nonparallel ordered tiling cannot exist, and complex patterns result.

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[25] Rhombus orientational order emerges at about the density at which hard pentagons freeze from a fluid into a rotator crystal; only at densities of about 84% do pentagons acquire orientational order [24]. The rhombus aspect ratio A controls its translational-orientational coupling; it would be interesting to determine for which A rhombi can display rotator- and liquid crystal phases.

[26] Ψ is an imperfect (though revealing) measure of order in systems without H-bond interactions. We verified that $\Psi \approx 0$ for (phantom) symmetric patches and for phantom patches placed under the peak of the curve in Fig. S3.

[27] A nonspecific forcefield of long range ($a_0 \gtrsim 1.8\,a$) favors energetically the *random* tiling.